(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 February 2002 (21.02.2002)

PCT

(10) International Publication Number
WO 02/14045 A1

(51) International Patent Classification[7]: B29C 45/00, A61M 5/31 // B29K 29:00

(21) International Application Number: PCT/GB01/03653

(22) International Filing Date: 15 August 2001 (15.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0020080.8 15 August 2000 (15.08.2000) GB

(71) Applicant *(for all designated States except US)*: **BOREALIS TECHNOLOGY OY** [FI/FI]; FIN-06101 Porvoo (FI).

(71) Applicant *(for GB only)*: **COCKBAIN, Julian** [GB/GB]; Flat 4, 83 Linden Gardens, London E2 4EU (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **MATTHIJS, Dirk** [BE/BE]; Hellemeersen 2, B-9910 Knesselone (BE). **JAMTVEDT, Svein** [NO/NO]; Blåværv. 1, N-3960 Stathelle (NO). **HÄRKÖNEN, Mika** [FI/NO]; Heggelia 18, N-3930 Porsgrunn (NO). **ØYSAED, Harry** [NO/NO]; Brattelia 1C, N-3960 Stathelle (NO).

(74) Agents: **JULIAN, Cockbain** et al.; Frank B. Dehn & Co., 179 Queen Victoria Street, London EC4V 4EL (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EC, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/14045 A1

(54) Title: PROCESS OF INJECTION MOULDING A SYRINGE FROM POLYTHYLENE WAX CONTAINING POLYPROPYLENE, SYRINGE OBTAINED THEREBY AND PARTICULATE COMPOSITION THEREFOR

(57) Abstract: The invention provides a syringe barrel formed by injection moulding of a polypropylene composition, characterised in that said polypropylene composition contains a polyethylene wax. The invention further provides a syringe having a barrel formed by injection moulding of a polypropylene composition, characterised in that said polypropylene composition contains a polyethylene wax and a polypropylene composition suitable for such moulding.

PROCESS OF INJECTION MOULDING A SYRINGE FROM POLYTHYLENE WAX CONTAINING POLYPROPYLENE, SYRINGE OBTAINED THERBY AND PARTICULATE COMPOSITION THEREFOR

This invention relates to improvements in and relating to the production of injection moulded polyolefin articles, in particular polypropylene articles, more especially syringes.

Syringes are frequently produced by injection moulding of polymers. The polymers used must provide a sufficiently low friction between the outer surface of the plunger and the inner surface of the syringe barrel. In the case of polypropylene, this low friction is conventionally achieved by including a slip agent (e.g. oleamide or erucamide) in the polymer composition used for injection moulding.

However the oleamide slip agent migrates towards the surface over a period of a few weeks and causes blooming, the formation of a hazy layer which decreases the transparency of the syringe.

We have now found that by including a polyethylene wax in the polypropylene, the slip agent can be used at concentrations at which the problem of blooming is reduced or eliminated.

Thus viewed from one aspect the invention provides a syringe barrel formed by injection moulding of a polypropylene composition, characterised in that said polypropylene composition contains a polyethylene wax.

Viewed from a further aspect the invention provides a syringe having a barrel formed by injection moulding of a polypropylene composition, characterised in that said polypropylene composition contains a polyethylene wax.

While the plungers in the syringes of the invention may be made of various materials, in particular polyolefins, the syringes of the invention preferably comprise plungers having a barrel contacting surface of HDPE, in particular plungers formed by injection

moulding of a HDPE composition, e.g. comprising HDPE having $MFR_{2.16}$ (190°C) of 7 to 40 and density 955 to 964 kg/m^3. (MFR may be measured according to ISO 1133).

The polypropylene compositions used in the production of the syringe barrels preferably contain a slip agent, i.e. a surface friction reducing agent. Suitable slip agents include amides of fatty acids, e.g. amides of C_{12} to C_{24} saturated or unsaturated fatty acids, including such amides of bis or polyamines, e.g. ethylene diamine. Examples of such amides include oleamide, erucamide, stearamide, ethylene-bis-stearamide, and ethylene-bis-oleamide, and mixtures thereof. Typically such slip agents will constitute 0.02 to 0.4 wt %, preferably 0.05 to 0.25 wt %, more preferably 0.1 to 0.20 wt % of the polypropylene compositions.

Oleamide is commercially available, for example as Crodamide OR from Croda Universal Ltd, Armoslip CP from Akzo Nobel or Atmer SA 1758 or 1759 from CIBA.

The polyethylene (PE) wax used according to the present invention will generally be a low molecular weight ethylene homo or copolymer, e.g. having a viscosity at 140°C of up to 100,000 mPas (e.g. 100 to 100 000 mPas or 10 000 to 90 000 mPas), preferably up to 50 000 mPas, (e.g. 12 000 to 45 000 mPas) more preferably between 500 to 35000 mPas, e.g. 15 000 to 35 000 mPas or 22 000 to 28 000 mPas, particularly about 25 000 mPas. Typically PE waxes with viscosity 25 000 mPas at 140°C, e.g. produced by Ziegler catalysed polymerization, have a number average molecular weight (Mn) of 5 to 6 kD and an $MFR_{2.16}$ (190°C) of 300-500 g/10 min. A viscosity of 100 000 mPas at 140°C corresponds to Mn about 8 kD and $MFR_{2.16}$ (190°C) about 100. In contrast, polyethylene "plastics" typically have $MFR_{2.16}$ (190°C) of below 80 g/10 min. corresponding to Mn of about 9 kD.

PE waxes are available commercially and can be

produced for example by high pressure polymerization processes or using Ziegler catalysed polymerization. Typically Ziegler catalysis produces relatively high density non-polar PE wax, e.g. with densities of 930 to 980 kg/m^3. The high pressure processes typically produce non-polar PE waxes of lower densities, e.g. 910 to 950 kg/m^3, but can also be used to produce polar PE waxes of higher density, e.g. up to 1050 kg/m^3.

While any PE wax can be used according to the invention, it is preferred to use non-polar PE waxes of density 920 to 980 kg/m^3, especially 940 to 970 kg/m^3. Typically the PE wax will constitute 0.1 to 10 wt %, preferably 0.2 to 4 wt %, more preferably 0.5 to 2 wt % (e.g. 1.25 to 2 wt%) of the polypropylene compositions.

Examples of suitable commercially available PE waxes include Licowax PE 190 and Licowax PE 520, available from Clariant.

The polypropylene compositions may contain other components as desired, e.g. anti-oxidants, stabilizers, acid scavengers, clarifying agents, coloring agents, anti-UV agents, nucleating agents, antistatic agents, etc. Typically these will be present at less than 2 wt % each, more preferably less than 0.5 wt %, relative to the total composition weight. Examples of such components include Irganox 1010 and Irgafos 168 (stabilizers from Ciba Specialty Chemicals), calcium stearate and synthetic hydrotalcite (e.g. DHT-4A from Kyowa Chemical Industry)(acid scavengers), and 1,3:2,4-di(ethylbenzylidene)sorbitol -EBDS (e.g. NC-4 from Mitsui Toatsu) and 1,3:2,4 bis (3,4-dimethylbenzylidene)sorbitol - DMDBS (e.g. Millad 3988 from Milliken Chemicals)(sorbitol clarifying agents).

The polypropylene used may be any propylene homo or copolymer suitable for injection moulding, especially clarified propylene homo and copolymers. Especially suitable are random propylene copolymers, e.g. containing up to 5% wt. comonomer, particularly 2 to 4%

wt. comonomer, e.g. α-olefin comonomer, particularly ethylene. Comonomers preferably do not include but-1-ene. The polypropylene preferably has $MFR_{2.16}$ (230°C) of 2 to 100 g/10 min, especially 10 to 50 g/10 min, more especially 15 to 30 g/10 min. Such polypropylenes are widely available commercially. The polypropylene preferably constitutes from 90 to 99.5 wt %, more preferably 97 to 99 wt % of the polypropylene composition.

Clarified polypropylenes can be produced for example by melt blending the polypropylene with clarifying or nucleating agents, for example sorbitol derivatives such as EDBS, MDBS (1,3:2,7-di(methyl-benzylidene)sorbitol), and DMDBS, phosphate salts (such as for example sodium 2,2'-methylenebis(4,6-di-tert.butylphenyl) phosphate), sodium benzoate, polyvinylcyclohexane, etc. Typically such clarifying or nucleating agents can result in haze levels immediately post injection moulding of below 60%, more preferably below 40%, in 2 mm thick injection moulded sheets.

The polypropylene compositions as described above form a further aspect of the invention.

Viewed from a further aspect the invention provides a process for the production of a syringe barrel comprising forming said barrel by injection moulding of a PE wax-containing polypropylene composition.

Viewed from a still further aspect the invention provides a particulate polypropylene injection moulding composition, said composition containing a PE wax and preferably also a slip agent.

The syringes according to the invention will typically have volumes, i.e. maximum injectable contents, of 0.1 to 300 mL, preferably 0.2 to 150 mL. The syringe shape may be any shape achievable by injection moulding and may be sold empty or pre-filled, e.g. with injectable liquids such as pharmaceuticals or contrast agents.

The syringe barrels of the invention will generally be cylindrical with an opening at one end for introduction of the plunger and with an opening or an openable vent at the other end through which the syringe contents may be expelled.

Injection moulding may be effected using equipment and conditions conventional for injection moulding of polypropylene.

The invention also extends to other transparent injection moulded polypropylene articles having friction surfaces, i.e., surfaces over which in use a further polymer article is intended to slide.

The invention will now be described further with reference to the following Examples.

EXAMPLE 1

Injection Moulding Composition

Polypropylene powder*	100 parts by weight
Oleamide (Crodamide OR)	0.15 parts by weight
PE-wax (Licowax PE190 from Clariant)	1.00 parts by weight
Irganox B215FF (Ciba)	0.15 parts by weight
DMDBS	0.2 parts by weight
Synthetic hydrotalcite	0.05 parts by weight

* random propylene ethylene copolymer containing 3% wt. ethylene

EXAMPLE 2

Injection Moulding

Syringe barrels and plungers for a 50 mL syringe were formed by injection moulding of the composition of Example 1 and of an HDPE respectively.

EXAMPLE 3

Coefficient of friction (COF), haze and visual appearance of injection moulded articles

2 mm thick polypropylene sheets were prepared by injection moulding a polypropylene composition according to the invention (substantially the same as the composition of Example 1) and a comparison composition containing no PE-wax and higher oleamide levels. The dynamic and static coefficients of friction for the sheets were determined and are set out in Table 1 below.

Table 1

Composition	Oleamide % wt.	PE-wax % wt.	Static COF	Dynamic COF
Invention	0.15	1.0	0.57	0.34
Comparison	0.25	0.0	0.60	0.34

As can be seen, the friction characteristics were substantially equivalent.

Such 2mm thick polypropylene sheets were annealed for 72 hours at 55°C to imitate normal "ageing" and the haze and visual appearance determined are set out in Table 2 below.

Table 2

Composition	Haze	Visual Appearance
Invention	42%	bare visible surface layer
Comparison	51%	clearly visible greasy surface layer

Claims

1. A syringe barrel formed by injection moulding of a polypropylene composition, characterised in that said polypropylene composition contains a polyethylene wax.

2. A barrel as claimed in claim 1 wherein said polyethylene wax has a viscosity at 140°C of up to 100000 mPas.

3. A barrel as claimed in claim 1 wherein said polyethylene wax has a viscosity at 140°C of 500 to 35000 mPas.

4. A barrel as claimed in claim 1 wherein said polyethylene wax has a viscosity at 140°C of 15 000 to 35 000 mPas.

5. A barrel as claimed in any one of claims 1 to 4 wherein said composition contains 0.1 to 10% weight of said polyethylene wax.

6. A barrel as claimed in any one of claims 1 to 5 wherein said composition further contains a slip agent.

7. A barrel as claimed in claim 6 wherein said composition contains 0.02 to 0.5% weight of said slip agent.

8. A barrel as claimed in any one of claims 1 to 7 wherein said composition contains a clarified polypropylene.

9. A barrel as claimed in any one of claims 1 to 8 wherein said polyethylene wax is Licowax PE 190 or Lycowax PE 250.

10. A process for the production of a syringe barrel comprising forming said barrel by injection moulding of a polypropylene composition characterised in that said polypropylene composition is as defined in any of claims 1 to 9.

11. A syringe having a barrel formed by injection moulding of a polypropylene composition, characterised in that said polypropylene composition is as defined in any of claims 1 to 9.

12. A syringe as claimed in claim 11 having a polyolefin plunger.

13. A syringe as claimed in claim 12 having an HDPE plunger.

14. A syringe as claimed in any one of claims 11 to 13 containing an injectable liquid.

15. A particulate polypropylene injection moulding composition, characterised in that said polypropylene composition is as defined in any of claims 1 to 9.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 01/03653

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B29C45/00 A61M5/31 //B29K23:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61M B29C C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data, RAPRA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 338 790 A (CHATTERJEE ANANDA M) 16 August 1994 (1994-08-16) column 1, line 24 column 7, line 54 -column 8, line 3 column 9, line 22; table 1	1-3,7,8, 10,11,15
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 039 (M-116), 10 March 1982 (1982-03-10) & JP 56 155730 A (TOA NENRYO KOGYO KK), 2 December 1981 (1981-12-02)	15
A	abstract	10

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 November 2001	16/11/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Nieuwenhuize, O

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 01/03653

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 10, 31 August 1998 (1998-08-31) & JP 10 139977 A (CHISSO CORP), 26 May 1998 (1998-05-26) abstract	15
A	WO 94 13345 A (MALLINCKRODT MEDICAL INC) 23 June 1994 (1994-06-23) page 4, paragraph 1	1,10,11
A	US 5 620 425 A (WELSHER ALLEN ET AL) 15 April 1997 (1997-04-15) example 1	1,10-12, 14
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 11, 28 November 1997 (1997-11-28) & JP 09 194648 A (TOKUYAMA CORP), 29 July 1997 (1997-07-29) abstract	8
A	DATABASE WPI Section Ch, Week 199315 Derwent Publications Ltd., London, GB; Class A96, AN 1993-120434 XP002181863 & JP 05 057018 A (TERUMO CORP), 9 March 1993 (1993-03-09) abstract	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte: ›nal Application No
PCT/GB 01/03653

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5338790 A	16-08-1994	AT 181347 T	15-07-1999
		AU 7397894 A	13-02-1995
		DE 69419179 D1	22-07-1999
		DE 69419179 T2	28-10-1999
		EP 0739381 A1	30-10-1996
		ES 2132420 T3	16-08-1999
		WO 9502638 A1	26-01-1995
JP 56155730 A	02-12-1981	JP 59050504 B	08-12-1984
JP 10139977 A	26-05-1998	NONE	
WO 9413345 A	23-06-1994	AU 5745494 A	04-07-1994
		WO 9413345 A1	23-06-1994
US 5620425 A	15-04-1997	AT 175381 T	15-01-1999
		AU 678610 B2	05-06-1997
		AU 7821594 A	23-05-1995
		CA 2151482 A1	11-05-1995
		CN 1115973 A ,B	31-01-1996
		DE 69415793 D1	18-02-1999
		DE 69415793 T2	02-09-1999
		DK 680401 T3	30-08-1999
		EP 0680401 A1	08-11-1995
		EP 0862979 A2	09-09-1998
		ES 2126784 T3	01-04-1999
		WO 9512482 A1	11-05-1995
		IL 111399 A	30-10-1998
		JP 8505334 T	11-06-1996
		ZA 9408179 A	08-08-1995
JP 09194648 A	29-07-1997	NONE	
JP 5057018 A	09-03-1993	NONE	